WASTES — UTILIZATION IN PRODUCTION

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CERAMIC PIGMENTS FOR CONSTRUCTION CERAMICS

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The possibility of synthesizing ceramic pigments using industrial wastes — nepheline sludge from the production of alumina, spent sulfovanadate diatomite (SVD) catalyst, and spent Ziegler – Natt catalyst — is studied. These materials will lower production costs of ceramic pigments. Nepheline sludge and spent catalysts make it possible to obtain on-glaze paints and ceramic pigments in the sand-color-brown-olive-green color range. The pigments synthesized are also recommended for volume coloring of ceramic pastes in the manufacture of construction materials.

Key words: utilization of wastes, spent catalysts, pigments, protective-decorative coatings, volume coloring of construction ceramic.

The present economic conditions make it imperative to lower the production costs, utilize raw materials fully, and develop waste-free methods of production. The construction industry requires inexpensive ceramic pigments suitable for obtaining protective-decorative coatings and for volume coloring of ceramic pastes. A timely problem is obtaining ceramic pigments based on inexpensive raw materials — industrial wastes, whose chemical composition is constant and which contain the required structure-forming oxides (oxides of titanium, aluminum, calcium, chromium, nickel, and others) and/or oxides-chromophores (oxides of iron, cobalt, chromium, nickel, and others). Examples of such wastes are a by-product of autoclave production of nickel, spent NTK-4 catalyst containing copper compounds as well as GIAP-10 and GIAP-16 catalysts containing zinc and nickel compounds, respectively, and various slags and sludges containing iron oxides and other compounds [1 – 3].

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The results of investigations of obtaining ceramic pigments using wastes from various production processes, specifically, nepheline sludge from the production of alumina, spent SVD catalyst, and spent Ziegler – Natt catalyst, are presented in this article.

Nepheline sludge, whose chemical composition is presented in Table 1, is a product of the processing of natural nepheline ores in the production of alumina.

The main component of the sludge is β-$2CaO \cdot SiO_2$, comprising 70 – 75%[3] of the sludge.

Nepheline sludge from the Achin Alumina Works is distinguished by its low content of calcium carbonates, comprising 3 – 4% on average. Noteworthy minor components of the sludge are calcium and sodium hydroaluminates, calcium hydroferrites and aluminum-ferrites, and iron hydroxide compounds.

Nepheline sludge was used to obtain and investigate ceramic pigments with wollastonite and diopside structure [4].

[3] Here and below — content by weight.

TABLE 1.

Initial material	Content by weight, %							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	R_2O	other
AGK nepheline sludge	29.12	3.67	4.55	53.20	1.45	–	3.06	4.96
Prosyanovskoe kaolin	46.73	37.43	0.72	0.71	0.65	0.47	0.18	13.12

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TABLE 2.

Pigment*	Chromophore	Chromophore content, wt.%	Color	Color coordinates			Wavelength, nm	Color purity, %
				x	*y*	*z*		
Pigments obtained from nepheline sludge								
A-2	CoO	6.5	Dark-blue	0.23	0.31	0.46	488	35
A-10	Cr_2O_3	12.3	Yellow-green	0.36	0.41	0.33	565	43
S-6	NiO	10.0	Yellow-sandy	0.41	0.36	0.33	591	37
S-16	Fe_2O_3	20.0	Brown	0.56	0.32	0.12	610	70
Pigments obtained from spent Ziegler – Natt complex								
Ts-2	CoO	10.0	Bluish-grey	0.21	0.24	0.55	481	33
Ts-6	NiO	20.0	Olive	0.36	0.46	0.18	561	60
Ts-7	Fe_2O_3	10.0	Yellow-brown	0.47	0.43	0.10	582	77
Pigments obtained from spend SVD catalyst								
PSh-1	CoO	5.0	Greenish-mustard	0.45	0.43	0.12	580	73
PSh-2	Fe_2O_3	15.0	Wine color	0.58	0.35	0.07	607	80

* Firing temperature 1150°C.

We investigated the possibility of synthesizing ceramic pigments with anortite and sphene structures according to the reactions:

$$2CaO \cdot SiO_2 + Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + SiO_2 + Al_2O_3 \rightarrow (CaO \cdot Al_2O_3 \cdot 2SiO_2); \quad (1)$$

$$2CaO \cdot SiO_2 + SiO_2 + 2TiO_2 \rightarrow 2(CaO \cdot TiO_2 \cdot SiO_2). \quad (2)$$

Kaolin from the Prosyanovskoe deposit and oxides of silicon, titanium, and aluminum were used as additives in the charge.

The chromophoric oxides CoO, NiO, Cr_2O, and Fe_2O_3 in the form of sulfate and nitrate salts were introduced into the mix in amounts 4 – 24% (in terms of the oxide). The pigments were fired at temperatures 1100 – 1200°C. The fired samples were comminuted to residue no greater than 0.2% on a No. 0063 sieve.

Visual analysis showed that many pigments synthesized according to the two reactions with one and the same chromophore differ in color. The color of the pigments depends on the structure of their crystal lattice and on the coordination of the chromophore ion. In the synthesized structures, the chromophore ions can occupy the Ca^{2+} and Ti^{4+} positions, whose coordination is octahedral, as well as the positions of Al^{3+}, which possesses tetrahedral coordination.

The color and color characteristics of the pigments are presented in Table 2. The cobalt-containing pigments synthesized according to the reaction (1) are blue and dark-blue and the pigments synthesized via the reaction (2) are blue-green and emerald-green. It is known that substances containing tetrahedral doubly-charged complex cobalt ions have a blue or green color while octahedral Co^{2+} complexes impart rose and lilac colors [5]. Therefore, cobalt ions in pigments obtained via both reactions possess tetrahedral coordination.

Pigments with nickel oxide which were obtained via the reaction (1) are grey and grey-green and pigments obtained via the reaction (2) have yellow-sandy and brown hues. In ceramic pigments, nickel in the form of the complexes $[NiO_4]$ imparts a blue color; nickel in form $[NiO_6]$ imparts a color that can vary from brown to yellow-brown and green. The color of the synthesized nickel-containing pigments attests to octahedral coordination of Ni^{2+}.

The coordination of Cr^{3+} ions is octahedral. The oxygen compounds of chromium can impart green, yellow, red, and rose colors. The color of chromium-containing pigments obtained via the reaction (1) varies from yellow- to grass-green or olive, while brownish green hues appear in pigments obtained via the reaction (2).

It should also be noted that the color of the pigments obtained is a manifestation of the chromophoric properties of the combination of iron oxide and other oxide chromophores, since nepheline sludge also contains 4.55% iron oxide.

Increasing the firing temperature to 1200°C has a negative effect on the color properties of the pigments. In addition, some pigments fuse, and it is difficult to grind the resulting agglomeration.

Diffractometric analysis of the pigments showed that the following crystalline phases formed as a result of synthesis via the reaction (1): anortite (dominant, $d = 0.408$, 0.321, and 0.213 nm) and mullite ($d = 0.341$, 0.221, and 0.169 nm). As temperature increases, the anortite diffraction peaks become more intense.

The phase composition of the sample obtained via the reaction (2) is represented by titanium oxide in the form of rutile ($d = 0.324$, 0.249, and 0.219 nm), sphene ($d = 0.298$, 0.285, and 0.209 nm), and pseudo-wollastonite ($d = 0.342$ and 0.198 nm). Sphene is not the dominant phase; the strongest diffraction peaks are due to rutile. Therefore, it can be

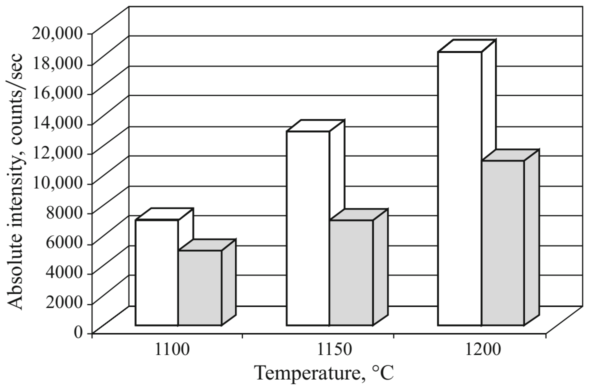

Fig. 1. Temperature variation of the absolute intensity of the diffraction peaks characteristic for sphene (d = 0.298 nm) and anortite (d = 0.320 nm).

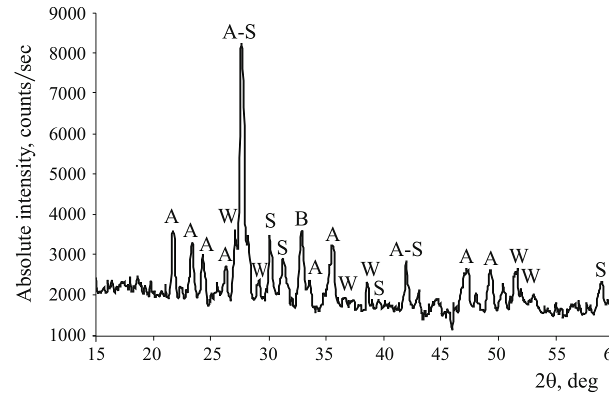

Fig. 2. Diffraction pattern of a blank sample, obtained by the scheme (3) using spent Ziegler – Natt catalytic complex (firing temperature 1200°C): A) anortite, S) sphene, W) wollastonite.

concluded that the synthesis temperature must be raised in order to attain a higher degree of completion of the reaction.

The temperature changes of the diffraction peaks which are characteristic for anortite and sphene are shown in Fig. 1.

The possibility of obtaining ceramic pigments containing anortite and sphene simultaneously by using spent Ziegler – Natt catalyst was investigated.

The spent Ziegler – Natt catalytic complex contains titanium chloride $TiCl_3(TiCl_4)$ and diethyl aluminum chloride. After it is neutralized a mixture of hydroxides $Al(OH)_3$ and $TiO(OH)_2$ (RF Patent No. 2184101) forms in the main product [6]. The catalyst brought to white heat at 600 – 800°C consists of a yellowish-white powder. In terms oxides the mixture contains 40 – 60% Al_2O_3 and 40 – 60% TiO_2.

Ceramic pigments with anortite and sphene structure were obtained according to the scheme

$$(TiO_2 + Al_2O_3) + 2(CaO \cdot SiO_2) + SiO_2 \longrightarrow CaO \cdot TiO_2 \cdot SiO_2 \quad + \quad CaO \cdot Al_2O_3 \cdot 2SiO_2 \qquad (3)$$

The spent Ziegler – Natt catalyst and the natural wollastonite were comminuted to residue not exceeding 2% on a No. 0063 sieve. Next, compositions with introduction of a chromophore were obtained according to the scheme (3). Chromophores in the form of cobalt, iron, chromium, and nickel salts were added in amounts 3.0 – 20.0% (in terms of oxides) to the mixture which contained 38.4% product of neutralization of the Ziegler – Natt catalyst, 49.0% wollastonite, and 12.6% silica. Boric acid was added in the amount 2% (above 100%) as a mineralizer. The mixture was fired at 1100 – 1200°C.

X-ray analysis of the pigments established that the crystal structure of samples obtained consists of multiple phases. Thus, a blank sample fired at 1200°C was found to contain anortite (d = 0.408, 0.380, and 0.320 nm), sphene (d = 0.320, 0.285, and 0.209 nm), and wollastonite (d = 0.331, 0.297, and 0.233 nm); in addition, the anortite and sphene (d = 0.320 nm) peaks overlap, forming a single dominating diffraction peak (Fig. 2).

In the diffraction patterns of the nickel-containing pigments, the intensity of the anortite peaks increases. As the content of nickel and iron oxides in the pigments increases to 10%, the oxides are fixed as the autonomous phases NiO (d = 0.240 and 0.208 nm) and Fe_2O_3 (d = 0.269 and 0.251 nm).

The presence of wollastonite in the reaction products attests that the reaction has not gone to completion. For this reason it is recommended that synthesis in this form be conducted at higher temperatures or that nonstoichiometric mixtures be used.

A similar reaction using nepheline sludge instead of wollastonite was conducted according to the scheme

$$(TiO_2 + Al_2O_3) + 2CaO \cdot SiO_2 + 2SiO_2 \longrightarrow CaO \cdot TiO_2 \cdot SiO_2 \quad + \quad CaO \cdot Al_2O_3 \cdot 2SiO_2 \qquad (4)$$

The results of the investigations are identical to those presented above. A visual examination showed that pigments synthesized according to the third and fourth schemes mainly have muddy hues. Consequently, it can be concluded that it is undesirable to use multiphase systems as the basis for ceramic pigments, since the chromophores occupying positions with different coordination give mixed tones, which degrades the color and lower the brightness and purity of tone.

The possibility of synthesizing ceramic pigments base of the wastes from the Kemerovo "Azot" JSC which consist of SVD catalyst (sulfovanadate on diatomite), whose formula is $35SiO_2 \cdot V_2O_5 \cdot 3K_2O \cdot 6SO_3$. The chemical composition of the spent SVD catalyst is 64.9% SiO_2, 6.2% V_2O_5, 5.2% Al_2O_3, 9.1% K_2O, and 14.6% SO_3.

The initial materials for SVD are naturally occurring diatomite, vanadium oxide V_2O_5, and potassium sulfate.

TABLE 3.

Pigment	Content, wt.%			Chromophore content, wt.%			
	SSVD	Al_2O_3	K_2O	Fe_2O_3	Cr_2O_3	CoO	NiO
P4 – P6	85 – 95	–	–	5 – 15	–	–	–
P7 – P9	85 – 95	–	–	–	5 – 15	–	–
P10 – P12	85 – 95	–	–	–	–	5 – 15	–
PSh_1	76.5	12.4	6.1	–	–	5	–
PSh_2	68.4	11.1	5.5	15	–	–	–
PSh_3	72.4	11.8	5.8	–	10	–	–
PSh_4	72.4	11.8	5.8	–	–	–	10
KhP	80.5	13.1	6.4	–	–	–	–

The spent SVD catalyst (SSVD) consists of granules ranging in color from yellow to light-brown. The color of the catalyst is due to vanadium oxide V_2O_5 distributed uniformly over the surface of the carrier (diatomite). Thus, SSVD contains a color-carrying oxide V_2O_5 and the structure-forming oxides SiO_2 and Al_2O_3.

Compositions based on that of spent SVD catalyst were made to obtain pigments. The investigations were performed in the following directions:

the action of the coloring salts added to SSVD in amounts 5 – 20% in terms of oxide (RF Patent No. 2255056) was studied;

the compositions with stoichiometry close to that of potassium feldspar were developed and studied.

The mix compositions of the pigments are presented in Table 3.

The spent SVD catalyst was first dried and comminuted to residue no more than 2% on a No. 0063 sieve. The comminuted SSVD was calcined at 800°C, after which compositions were made using SSVD and other components. Cobalt, nickel, iron, manganese, chromium, and copper oxides were introduced into the mix by means of salts in amounts 5 – 15% (in terms of the oxides). The mixtures were moistened for better dissolution of the salts in the mix and then dried and calcined at temperatures ranging from 800 to 950°C with soaking for 30 min at the maximum temperature. The low calcination temperature of the pigments is explained by the presence of K_2O as a flux in the SSVD composition.

After calcination the pigments were comminuted to residue not more than 0.2% on a No. 0063 sieve.

Visual examination showed that the pigments synthesized at 850°C possess the most saturated colors. The color of the pigments varies from red-brown and sandy to yellow-green, grass color, and turquoise. In general, these are different hues of sandy and olive colors.

XPA data show that amorphous silica and crystalline phases — potassium silicate K_2SiO_3 ($d = 0.302$, 0.262, and 0.243 nm) and potassium vanadium oxide sulfate $K_3V_2O_2(SO_4)_4$ ($d = 0.781$, 0.405, and 0.356 nm) — are present in the catalyst heated at 800°C.

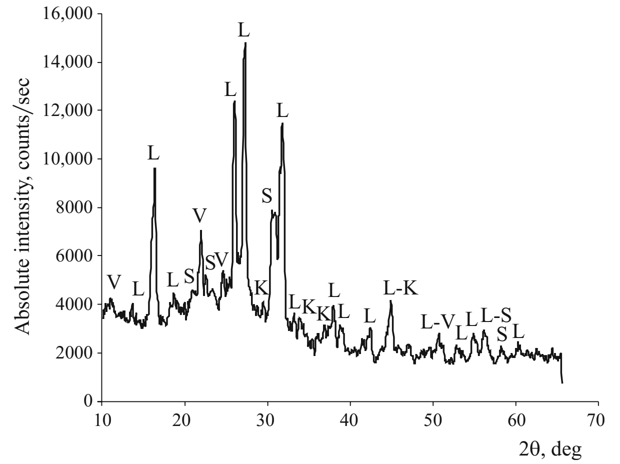

Fig. 3. Diffraction pattern of a blank sample based on spent SVD catalyst (calcination temperature 850°C): L) leucite, K) K_2SiO_3, S) K_2SO_4, V) $K_3V_2O_2(SO_4)_4$.

When projecting the structure of potassium feldspar (PFS), leucite ($d = 0.540$, 0.343, 0.328, and 0.281 nm) as well as potassium silicate K_2SiO_3 ($d = 0.302$, 0.262, and 0.243 nm), potassium sulfate K_2SO_4 ($d = 0.413$, 0.393, and 0.288 nm), and $K_3V_2O_2(SO_4)_4$ ($d = 0.781$, 0.405, and 0.356 nm) are indentified instead PFS in the diffraction patterns of the samples (Fig. 3).

The pigments synthesized using nepheline sludge, spent Ziegler – Natt catalyst, and spent SVD catalyst were tested as on-glaze paints and for obtaining colored glazes. In the first case, the pigments were mixed with flux and deposited on the surface of glazed articles, which were then fired at 850°C. The color of the on-glaze paints remained essentially unchanged; only the brighter hues came through. To obtain decorative-protective glassy coatings on construction ceramic the pigments were introduced into tile glazes.

In summary, it is cost-effective to use industrial wastes to synthesize ceramic pigments, since the production costs of the pigments decrease. Nepheline sludge and spent Ziegler – Natt catalyst added in different amounts to the mixes make it possible to obtain derivative crystalline structures, thereby expanding the color palette of ceramic pigments. Spent SVD catalyst possesses a yellow color because of the vanadium oxide present in the catalyst, and adding other chromophores gives a series of ceramic pigments with sandy-brown-olive colors.

The pigments based on nepheline sludge and spent SVD catalyst melt at low temperatures, which determines the applications of the pigments — to obtain on-glaze paints and protective-decorative coatings for construction ceramics. Pigments synthesized using spent Ziegler – Natt catalyst are more stable at high temperatures and can be used as subglaze paints. In addition, the pigments obtained on the basis of inexpensive initial materials can be used for volume coloring of ceramic pastes in the production of construction materials.

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